FORM PTO-1390 (Modified) (REV 11-2000) U.S. DEPARTMENT OF COMMERCE, PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	
4004-022-30	
U S APPLICATION NO. (IF KNOWN, SEE 37 CFR	
09/914043	
INTERNATIONAL APPLICATION NO	INTERNATIONAL FILING DATE
PCT/EP00/01394	21 FEBRUARY 2000
PRIORITY DATE CLAIMED	
24 FEBRUARY 1999	

TITLE OF INVENTION

BLUE SODIOCALCIC GLASS

APPLICANT(S) FOR DO/EO/US

Dominique COSTER; Laurent DELMOTTE and Marc FOGUENNE

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include itens (5), (6), (9) and (24) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   a. ☒ is attached hereto (required only if not communicated by the International Bureau).
   b. ☐ has been communicated by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☒ is attached hereto.
   b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   b. ☐ have been communicated by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. A copy of the International Search Report (PCT/ISA/210).

13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

Verification of English language translation

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
09/914043	PCT/EP00/01394	4004-022-30

24. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

		CALCULATIONS PTO USE ONLY
☐	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1000.00**	
☒	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$860.00**	
☐	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$710.00**	
☐	International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**	
☐	International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**	
	ENTER APPROPRIATE BASIC FEE AMOUNT =	**$860.00**
	Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	**$130.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	13 - 20 =	0	x $18.00	**$0.00**
Independent claims	1 - 3 =	0	x $80.00	**$0.00**
Multiple Dependent Claims **(check if applicable).**			☐	**$0.00**
	TOTAL OF ABOVE CALCULATIONS =			**$990.00**
Reduction for applicant claims small entity status. (See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				**$0.00**
	SUBTOTAL =			**$990.00**
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).			+	**$0.00**
	TOTAL NATIONAL FEE =			**$990.00**
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) **(check if applicable).** ☐				**$0.00**
	TOTAL FEES ENCLOSED =			**$990.00**
			Amount to be: refunded	$
			charged	$

a. ☒ A check in the amount of **$990.00** to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **50-1442** A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Supervisor, Patent Prosecution Services
PIPER MARBURY RUDNICK & WOLFE LLP
1200 Nineteenth Street, N.W.
Washington, D.C. 20036-2412

SIGNATURE

Jerold I. Schneider
NAME

24,765
REGISTRATION NUMBER

August 22, 2001
DATE

DOCKET NO. 4004-022-30

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: **COSTER et al**
SERIAL NO.: NEW PATENT APPLICATION
FILING DATE: HEREWITH
INT'L APPLN **PCT/EP00/01394**
INT'L FILING **FEBRUARY 21, 2000**
FOR: **BLUE SODIOCALCIC GLASS**

ART UNIT:
EXAMINER:

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to assigning a serial number and for fee calculation purposes, please amend this application as follows:

IN THE TITLE:

Change the title from "Blue Sodiocalcic Glass" to - - BLUE SODA-LIME GLASS - -

IN THE SPECIFICATION:

Page 1, prior to line 3, insert

- - CROSS-REFERENCE TO RELATED APPLICATIONS

This is the entry into the U.S. National Stage of PCT Application No. PCT/EP00/01394 filed 21 February 2000, claiming priority from European Application No. EP 99103543.7 filed 24 February, 1999, the disclosures of both of which are hereby incorporated by reference.

BACKGROUND OF THE INVENTION - -

Page 4, between lines 20 and 21 insert:

- - SUMMARY OF THE INVENTION - -

Page 13, between lines 28 and 29 insert:

- - DETAILED DESCRIPTION - -

IN THE CLAIMS:

Cancel claims 1-21 without prejudice and substitute the following new claims 22 through 34.

--22. A blue soda-lime colored glass composed of glass-forming principal components and of coloring agents, characterized in that it comprises from 0.15 to 1.1% by weight of Fe_2O_3, has a redox factor not exceeding 45% and presents a dominant wavelength (λ_D) of between 490 and 493 nm and a light transmission (TLA4) and an excitation purity (P) which satisfy the relationship $P > -0.3 \times TLA4 + 24.5$.

23. The colored glass as claimed in Claim 22 and further including at least one of the following features (A) through (D)

(A) a light transmission (TLA4) of greater than or equal to 55%;

(B) a light transmission (TLA4) and an excitation purity (P) which satisfy the relationship $P > -0.3 \times TLA4 + 26.5$;

(C) as coloring agents, a compound of at least one of the elements Cr, Ce, Co, Se, V, Ti, Mn; and

(D) it comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.3 – 1.1%
FeO	0.10 - 0.30%
Co	0 – 0.0040%
Cr_2O_3	0 – 0.0500%
V_2O_5	0 – 0.0500%

and has the following optical properties:

$55\% < TLA4 < 85\%$

36% < TE4 < 60%

P < 12%.

24. The colored glass as claimed in Claim 23 and further including at least two of the features (A) through (D).

25 The colored glass as claimed in Claim 23 and further including all of the features (A) through (D).

26. The colored glass as claimed in Claim 22 and further including at least one of the following features (E) through (G)

(E) it comprises amongst its coloring agents less than 0.1% by weight of TiO_2;

(F) it comprises less than 0.5% by weight of CeO_2;

(G) it comprises less than 0.13% by weight of MnO_2.

27. The colored glass as claimed in Claim 22, characterized in that it has a light transmission (TLA4) of greater than or equal to 70%.

28. The colored glass as claimed in Claim 23 wherein it further comprises one of the following features (H) through (K):

(H) the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.3 – 0.7%
FeO	0.10 - 0.20%
Co	0 – 0.0020%

and has the following optical properties:

72% < TLA4 < 85%

49% < TE4 < 60%

3% < P < 9%;

(I) the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.4 – 0.6%
FeO	0.11 - 0.16%
Co	0 – 0.0015%

and has the following optical properties:

74% < TLA4 < 80%

51% < TE4 < 58%

3% < P < 7%

$\lambda_D \leq 492$ nm;

(J) the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.4 – 0.8%
FeO	0.16 - 0.23%
Co	0 – 0.0030%

and has the following optical properties:

70% < TLA4 < 77%

39% < TE4 < 50%

4% < P < 10%; or

(K) the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.55 – 0.75%
FeO	0.16 - 0.23%
Co	0 – 0.0020%

and has the following optical properties:

70% < TLA4 < 74%

41% < TE4 < 48%

6% < P < 9%

$\lambda_D \leq 492$ nm.

29. The colored glass as claimed in claim 22, characterized in that it has a light transmission (TLA4) of less than 70%.

30. The colored glass as claimed in claim 22, further characterized by one of the following (L) through (N):

(L) it comprises less than 0.01%, preferably less than 0.0050%, by weight of V_2O_5 and less than 0.0020%, preferably less than 0.0015%, by weight of Cr_2O_3;

(M) it comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.6 – 1.1%
FeO	0.20 - 0.30%
Co	0 – 0.0040%

and has the following optical properties:

55% < TLA4 < 69%

30% < TE4 < 47%

6% < P < 12%;

(N) it comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.75 – 0.95%
FeO	0.22 - 0.28%
Co	0 – 0.0030%

and has the following optical properties:

$63\% < TLA4 < 69\%$

$36\% < TE4 < 45\%$

$7\% < P < 11\%$

$\lambda_D \leq 492$ nm.

31. The colored glass as claimed in Claims 22, characterized in that it forms a motor-vehicle window.

32. The colored glass as claimed in Claim 22 further characterized by a dominant wavelength (λ_D) of greater than or equal to 491 nm.

33. The colored glass as claimed in Claim 22 further characterized by a dominant wavelength (λ_D) of less than or equal to 492 nm.

34. The colored glass as claimed in Claim 22 further characterized in that it comprises less than 1.0% by weight of Fe_2O_3. - -

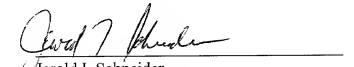
REMARKS

Claims 21 through 34 are pending in this application. The application has been amended to conform to U.S. practice and the claims have been amended to, *inter alia*, present claims without multiple dependency.

Favorable consideration is solicited.

Respectfully submitted,

PIPER MARBURY RUDNICK & WOLFE LLP



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Blue soda-lime glass

The present invention relates to a blue colored soda-lime glass composed of glass-forming principal constituents and of coloring agents.

The expression "soda-lime glass" is used here in the wide sense and relates to any glass which contains the following constituents (in percentages by weight):

Na_2O	10 to 20%
CaO	0 to 16%
SiO_2	60 to 75%
K_2O	0 to 10%
MgO	0 to 10%
Al_2O_3	0 to 5%
BaO	0 to 2%
BaO + CaO + MgO	10 to 20%
K_2O + Na_2O	10 to 20%.

This type of glass is very widely used in the field of glazing for buildings or automobiles, for example. It is usually manufactured in the form of a ribbon by the float process. Such a ribbon can be cut into sheets which can then be bent or can undergo a treatment to improve their mechanical properties, for example a thermal toughening step.

It is generally necessary to relate the optical properties of a glass sheet to a standard illuminant. In the present description, 2 standard illuminants are used, namely illuminant C and illuminant A defined by the Commission Internationale de l'Eclairage (C.I.E.). Illuminant C represents average daylight having a color temperature of 6700 K. This illuminant is especially useful for evaluating the optical properties of glazing intended for buildings. Illuminant A represents the radiation of a Planck radiator with a temperature of about 2856 K. This illuminant describes the light

emitted by car headlights and is essentially intended to evaluate the optical properties of windows intended for automobiles. The Commission Internationale de l'Eclairage has also published a document entitled "Colorimétrie, Recommandations Officielles de la C.I.E. [*Colorimetry and Official Recommendations of the C.I.E.*]" (May 1970) which describes a theory in which the colorimetric coordinates for light of each wavelength of the visible spectrum are defined so as to be able to be represented on a diagram having orthogonal axes x and y, called the C.I.E. chromaticity plot. This chromaticity plot shows the locus representative of light of each wavelength (expressed in nanometers) of the visible spectrum. This locus is called the "spectrum locus" and light whose coordinates lie on this spectrum locus is said to have 100% excitation purity for the appropriate wavelength. The spectrum locus is closed by a line called the purple boundary which connects the points of the spectrum locus whose coordinates correspond to wavelengths of 380 nm (violet) and 780 nm (red). The area lying between the spectrum locus and the purple boundary is that available for the chromaticity coordinates of any visible light. The coordinates of the light emitted by illuminant C, for example, correspond to $x = 0.3101$ and $y = 0.3162$. This point C is regarded as representing white light and consequently has an excitation purity equal to zero for any wavelength. Lines may be drawn from the point C to the spectrum locus at any desired wavelength and any point lying on these lines may be defined not only by its x and y coordinates but also as a function of the wavelength corresponding to the line on which it lies and as a function of its distance from the point C relative to the total length of the wavelength line. Consequently, the color of the light transmitted by a colored glass sheet may be described by its dominant wavelength and its excitation purity expressed as a percentage.

The C.I.E. coordinates of light transmitted by a colored glass sheet will depend not only on the composition of the glass but also on its thickness. In the present description, and in the claims, all the values of the excitation purity P and of the dominant wavelength λ_D of the transmitted light are calculated from the spectral specific internal transmissions (SIT_λ) of a glass sheet 5 mm in thickness. The spectral specific internal transmission of a glass sheet is governed solely by the absorption of the glass and can be expressed by the Beer-Lambert law:

$SIT_\lambda = e^{-E.A_\lambda}$ where A_λ is the absorption coefficient (in cm^{-1}) of the glass at the wavelength in question and E is the thickness (in cm) of the glass. To a first approximation, SIT_λ may also be represented by the formula:

$$(I_3 + R_2)/(I_1 - R_1)$$

where I_1 is the intensity of the visible light incident on a first face of the glass sheet, R_1 is the intensity of the visible light reflected by this face, I_3 is the intensity of the visible light transmitted from the second face of the glass sheet and R_2 is the intensity of the visible light reflected by this second face toward the interior of the sheet.

In the description which follows and in the claims, the following are also used:

- for illuminant A, the total light transmission (TLA) measured for a thickness of 4 mm (TLA4). This total transmission is the result of the integration between the 380 and 780 nm wavelengths of the expression: $\Sigma\ T_\lambda.E_\lambda.S_\lambda/\Sigma\ E_\lambda.S_\lambda$ in which T_λ is the transmission at the wavelength λ, E_λ is the spectral distribution of illuminant A and S_λ is the sensitivity of the normal human eye as a function of the wavelength λ;

- the total energy transmission (TE), measured for a thickness of 4 mm (TE4). This total transmission is the result of the integration between the 300 and

2500 nm wavelengths of the expression: $\Sigma T_\lambda . E_\lambda / \Sigma E_\lambda$ in which E_λ is the spectral energy distribution of the sun at 30° above the horizon;

- the selectivity (SE), measured as the ratio of the total light transmission for illuminant A to the total energy transmission (TLA/TE);

- the total transmission in the ultraviolet, measured for a thickness of 4 mm (TUV4). This total transmission is the result of the integration between 280 and 380 nm of the expression: $\Sigma T_\lambda . U_\lambda / \Sigma U_\lambda$ in which U_λ is the spectral distribution of the ultraviolet radiation that has passed through the atmosphere, defined in the DIN 67507 standard.

The redox ratio, which represents the value of the Fe^{2+}/total Fe ratio and is obtained by the formula:

$$Fe^{2+}/\text{total Fe} = [24.4495 \times \log(92/\tau_{1050})]/t\text{-}Fe_2O_3$$

where τ_{1050} represents the specific internal transmission of the 5 mm-thick glass at the 1050 nm wavelength and $t\text{-}Fe_2O_3$ represents the total iron content expressed in Fe_2O_3 oxide form and measured by X-ray fluorescence.

The present invention relates in particular to blue glasses. These glasses can be used in architectural applications and as glazing for railway carriages and motor vehicles. In architectural applications, glass sheets 4 to 6 mm in thickness are generally used while in the motor-vehicle field thicknesses of 1 to 5 mm are normally employed, particularly for the production of monolithic glazing, and thicknesses of between 1 and 3 mm in the case of laminated glazing, especially for windshields, two glass sheets of this thickness then being bonded together by means of an interlayer film, generally made of polyvinyl butyral (PVB).

The present demand for blue glazing is focused on products having, for a given light transmission level, a pronounced coloration, that is to say a high excitation purity, even for high light transmission levels, while still providing moderate transmission

levels for ultraviolet and infrared radiation.

Thus, FR 269 526 proposes blue glasses exhibiting these properties. However, they are only obtained at the cost of a high redox factor, of greater than 50%, which makes the glass highly heat-absorbant and consequently difficult to melt and to refine in conventional industrial furnaces, or of a high dominant wavelength of at least 494 nm, which corresponds, in particular for a glass having a high light transmission, to a shade of color tending toward green.

The invention eliminates these problematic drawbacks and provides a blue soda-lime colored glass composed of glass-forming principal components and of coloring agents, characterized in that it comprises from 0.15 to 1.1% by weight of Fe_2O_3, has a redox factor not exceeding 45% and presents a dominant wavelength (λ_D) of between 490 and 493 nm and a light transmission (TLA4) and an excitation purity (P) which satisfy the relationship $P > -0.3 \times TLA4 + 24.5$.

The glass according to the invention therefore has a high purity for a given light transmission and a pronounced blue shade of color, even for high light transmission levels, while still being able to be easily obtained in conventional industrial glass furnaces.

In addition, the glasses according to the invention have the advantage of combining a blue color with a high selectivity. A selectivity $S > 1.3$ is easily attained. This property is particularly advantageous both for motor vehicle applications and architectural applications, since it makes it possible to limit the heating due to solar radiation and therefore to increase the thermal comfort of the occupants of the vehicle or of the building.

It is advantageous for the glass according to the invention to have a redox ratio of less than 40%, thereby making the glass particularly easy to produce.

Preferably, the glass according to the

invention presents a light transmission of greater than or equal to 55%, which means that it can be used in most architectural applications or as vehicle windows.

This glass also preferably has a light transmission and an excitation purity which satisfy the relationship $P > -0.3 \times TLA4 + 26.5$, that is to say an even higher purity, for all light transmission levels. This clearly corresponds to the currently accepted criteria as regards esthetics.

Advantageously, the glass according to the invention presents a dominant wavelength of less than or equal to 492 nm, corresponding to a highly pronounced blue shade, particularly desirable from an esthetic standpoint. Likewise, esthetic considerations may make it desirable that the dominant wavelength of these glasses be greater than or equal to 491 nm, so that the shade of blue obtained is especially pleasing to the eye.

In certain forms of the invention, the glass presents a selectivity of at least 1.3, preferably at least 1.5. This makes it possible, for a given light transmission, to limit the heating of volumes bounded by windows using this glass.

Preferably, the glass according to the invention includes, as coloring agent, at least one of the elements chromium, cobalt, titanium, selenium, cerium, manganese and vanadium. The use of these elements allows the optical properties of the glass to be optimally adjusted and helps to obtain a glass having the desired shade and intensity of color.

Iron is present in most glasses existing on the market, either as an impurity or deliberately introduced as a coloring agent. The presence of Fe^{3+} gives the glass a slight absorption of visible light of short wavelength (410 and 440 nm) and a very strong absorption band in the ultraviolet (absorption band centered on 380 nm), whereas the presence of Fe^{2+} ions causes a strong absorption in the infrared (absorption

band centered on 1050 nm). The ferric ions give the glass a slight yellow coloration, whereas the ferrous ions give a more pronounced blue-green coloration. All other considerations being equal, it is the Fe^{2+} ions which are responsible for the absorption in the infrared range and which therefore determine TE. The value of TE decreases, thereby increasing the value of SE, as the concentration of Fe^{2+} ions increases. By favoring the presence of Fe^{2+} ions over Fe^{3+} ions, a high selectivity is therefore obtained.

The effects of the various other coloring agents individually envisaged for producing a glass are the following (according to "Le Verre" [*Glass*] by H. Scholze, translated by J. Le Dû, Institut du Verre [*Glass Institute*], Paris):

Cobalt: the $Co^{II}O_4$ group produces an intense blue coloration with a dominant wavelength almost opposite to that produced by the iron-selenium chromophor.

Chromium: the presence of the $Cr^{III}O_6$ group gives rise to absorption bands at 650 nm and a light green color. More extensive oxidation gives rise to the $Cr^{VI}O_4$ group which creates a very intense absorption band at 365 nm and gives a yellow coloration.

Cerium: the presence of cerium ions in the composition makes it possible to obtain a strong absorption in the ultraviolet range. Cerium oxide exists in two forms: Ce^{IV} absorbs in the ultraviolet around 240 nm and Ce^{III} absorbs in the ultraviolet around 314 nm.

Selenium: the Se^{4+} cation has virtually no coloring effect, whereas the uncharged element Se0 gives a pink coloration. The Se^{2-} anion forms a chromophor with the ferric ions present and consequently gives the glass a brown-red color.

Vanadium: for increasing contents of alkali metal oxides, the color changes from green to colorless, this being caused by the oxidation of the

$V^{III}O_6$ group into $V^{V}O_4$.

Manganese: appears in the glass in the form of practically colorless $Mn^{II}O_6$. The $Mn^{III}O_6$ group in glasses rich in alkali metals creates, however, a violet color.

Titanium: TiO_2 in the glasses gives them a yellow coloration. In large amounts, it is even possible to obtain, by reduction, the $Ti^{III}O_6$ group, which gives the glass a violet or even maroon color.

The energy and optical properties of a glass containing several coloring agents are therefore the result of a complex interaction between them. This is because, the behavior of these coloring agents depends greatly on their redox state and therefore on the presence of other elements liable to influence this state.

Preferably, the glass according to the invention comprises less than 0.1% by weight of TiO_2. A higher amount of TiO_2 runs the risk of giving the glass a yellow coloration which goes counter to the shade desired here.

It is also preferable for the glass according to the invention to contain less than 0.5% by weight CeO_2 amongst its coloring agents, since this element, which absorbs radiation in the ultraviolet, can be used to reduce the transmission of the glass in this wavelength range, although it results in a shift in the dominant wavelength toward the green. This shift may be corrected by increasing the redox ratio of the glass, but with the result that the glass is difficult to melt, as indicated above. Moreover, Ce is a very expensive element and its use in the glass, even in amounts not exceeding 1% by weight of CeO_2, may double the cost of the batch materials needed for its manufacture.

Advantageously, the glass according to the invention comprises no more than 0.13% of MnO_2 among its coloring agents. MnO_2 has an oxidizing character which

runs the risk of creating a green shade by modifying the redox state of the iron if it is used in a higher amount.

It is also desirable for this glass not to contain fluorocompounds among its coloring agents or at least for these not to represent more than 0.2% by weight of the glass. This is because these compounds give rise to discharges from the furnace which are environmentally very harmful and are, in addition, highly corrosive with respect to the blocks of refractory materials which line the inside of said furnace.

Moreover, it is preferred that the glass according to the invention be obtained from a mixture of principal glass-forming constituents with a concentration of MgO of greater than 2% since this compound encourages the melting of said constituents.

In preferred forms of the invention, the glass comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.3 - 1.1%
FeO	0.10 - 0.30%
Co	0 - 0.0040%
Cr_2O_3	0 - 0.0500%
V_2O_5	0 - 0.0500%

and has the following optical properties:

$55\% < TLA4 < 85\%$

$36\% < TE4 < 60\%$

$P < 12\%$.

Glasses having such characteristics are particularly suitable for a large number of motor-vehicle and architectural applications. The optical properties obtained correspond to selective products, that is to say to products having, for a given light transmission level, a low energy transmission level. This limits the extent to which volumes bounded by glazing manufactured from such glasses are heated up.

The transmission purity thus defined is also suitable for such applications.

For certain applications of the invention, particularly in the motor vehicle field, it is preferable for the glasses according to the invention to have a light transmission of greater than 70%, the lower limit of the official standards relating to front side windows of cars, or 75%, in the case of vehicle windshields.

Glasses particularly suitable for the manufacture of motor vehicle glazing, in particular windshields, comprise the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.3 - 0.7%
FeO	0.10 - 0.20%
Co	0 - 0.0020%

and has the following optical properties:

$72\% < TLA4 < 85\%$

$49\% < TE4 < 60\%$

$3\% < P < 9\%$.

Even more preferably, for such applications, the glass according to the invention comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.4 - 0.6%
FeO	0.11 - 0.16%
Co	0 - 0.0015%

and has the following optical properties:

$74\% < TLA4 < 80\%$

$51\% < TE4 < 58\%$

$3\% < P < 7\%$

$\lambda_D \leq 492$ nm.

For uses of the glass according to the invention as glazing for buildings or as front side windows of vehicles, it comprises the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.4 - 0.8%
FeO	0.16 - 0.23%
Co	0 - 0.0030%

and has the following optical properties:

70% < TLA4 < 77%

39% < TE4 < 50%

4% < P < 10%.

For such applications, it is particularly preferred that this glass comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.55 - 0.75%
FeO	0.16 - 0.23%
Co	0 - 0.0020%

and has the following optical properties:

70% < TLA4 < 74%

41% < TE4 < 48%

6% < P < 9%

$\lambda_D \leq 492$ nm.

For applications of the glass according to the invention as rear side windows of vehicles and in certain architectural applications allowing lower light transmission, this going hand in hand with a reduction in the energy transmission of the window, which may be extremely valuable in hot climates, this glass advantageously has a light transmission (TLA4) of less than 70%.

In this case, it is possible and preferable, for reasons of ease of manufacture and for reasons of reducing the cost of the batch materials needed for this manufacture, for the glass according to the invention to comprise less than 0.01%, preferably less than 0.0050%, by weight of V_2O_5 and less than 0.0020%, preferably less than 0.0015%, by weight of Cr_2O_3.

For these applications it is preferred that the glass according to the invention comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of

Fe_2O_3:

Fe_2O_3	0.6 - 1.1%
FeO	0.20 - 0.30%
Co	0 - 0.0040%

and has the following optical properties:

55% < TLA4 < 69%

30% < TE4 < 47%

6% < P < 12%.

Even more preferably, for the same applications, the glass according to the invention comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.75 - 0.95%
FeO	0.22 - 0.28%
Co	0 - 0.0030%

and has the following optical properties:

63% < TLA4 < 69%

36% < TE4 < 45%

7% < P < 11%

$\lambda_D \leq 492$ nm.

The light transmission range thus defined makes the glass according to the invention particularly useful for preventing the dazzling effect of the light from motor vehicle headlights when it is used for rear side windows or as rear windows of vehicles. The corresponding energy transmission range gives the glass its high selectivity.

For the purpose of making it easier to melt the glasses according to the invention, it is desirable for them to comprise amongst their coloring agents less than 1.0% by weight of Fe_2O_3.

The glass according to the invention may be coated with a layer of metal oxides which reduce the extent to which it is heated up by solar radiation and consequently the extent to which the passenger compartment of a vehicle using such glass as glazing is heated up.

The glasses according to the invention can be manufactured by conventional processes. As batch materials, it is possible to use natural materials, recycled glass, slag or a combination of these materials. The colorants are not necessarily added in the form indicated, but this way of giving the amounts of coloring agents added, in equivalents in the forms indicated, corresponds to the standard practice. In practice, the iron is added in the form of red iron oxide, the cobalt is added in the form of the hydrated sulfate, such as $CoSO_4 \cdot 7H_2O$ or $CoSO_4 \cdot 6H_2O$, and the chromium is added in the form of the dichromate such as $K_2Cr_2O_7$. The cerium is introduced in the form of the oxide or carbonate. As regards the vanadium, this is introduced in the form of the oxide or of sodium vanadate. The selenium, when it is present, is added in elemental form or in the form of the selenite such as Na_2SeO_3 or $ZnSeO_3$.

Other elements are sometimes present as impurities in the batch materials used to manufacture the glass according to the invention, whether in natural materials, in recycled glass or in slag, but when these impurities do not give the glass properties lying outside the limits defined above, these glasses are regarded as being in accordance with the present invention. The present invention will be illustrated by the following specific examples of optical properties and compositions

EXAMPLES 1 to 59

Table I gives by way of non-limiting indication the base composition of the glass and the constituents of the batch to be melted in order to produce the glasses according to the invention. Table II gives the proportions of coloring agents and the optical properties of glasses according to the invention. Table III gives by way of comparison with the glasses of the

invention examples of blue glasses tending toward green. The abovementioned proportions are determined by X-ray fluorescence of the glass and converted into the molecular species indicated.

The batch may, if necessary, contain a reducing agent such as coke, graphite, slag or an oxidizing agent such as a nitrate. In this case, the proportions of the other materials are adapted so that the composition of the glass remains unchanged.

TABLE I

Composition of the base glass		Constituents of the base glass	
SiO_2	71.5 to 71.9%	Sand	571.3
Al_2O_3	0.8%	Feldspar	29.6
CaO	8.8%	Lime	35.7
MgO	4.2%	Dolomite	167.7
Na_2O	14.1%	Na_2CO_3	189.4
K_2O	0.1%	Sulfate	5.0
SO_3	0.05 to 0.45%		

TABLE II

Ex. No.	Fe_2O_3 (%)	FeO (%)	Redox (%)	Co (ppm)	TLA4 (%)	TE4 (%)	TUV4 (%)	SE4	λ_D (nm)	P (%)
1	0.89	0.22	27.8	20	63.8	40.3	16.5	1.58	491.3	8.7
2	0.87	0.26	33.2	19	62.2	37.4	17.6	1.66	490.3	10.3
3	0.62	0.14	25.2	17	72.4	52.2	25.8	1.38	490.3	6.5
4	0.76	0.21	31.0	16	66.2	42.3	20.2	1.56	490.2	9.0
5	0.38	0.08	23.6	9	80.3	64.5	36.5	1.24	490.0	4.2
6	0.39	0.08	24.5	8	79.7	63.1	35.1	1.26	490.3	4.4
7	0.51	0.12	27.1	7	76.6	56.2	30.8	1.36	491.0	5.3
8	0.40	0.08	22.7	5	81.5	64.8	35.3	1.25	492.9	3.3
9	0.50	0.13	28.6	4	77.7	55.8	30.8	1.39	492.3	4.9
10	0.50	0.12	26.6	10	76.9	56.8	31.4	1.35	490.2	5.3
11	0.50	0.118	26.2	6	78.2	57.5	31.4	1.36	492.2	4.4
12	0.48	0.118	27.3	4	78.9	57.8	32.2	1.36	492.5	4.3
13	0.56	0.132	26.1	8	76.2	54.9	29.0	1.38	492.0	5.0
14	0.56	0.132	26.1	12	75.0	54.5	29.0	1.37	490.3	5.8
15	0.50	0.134	29.7	5	77.3	55.3	31.5	1.39	491.4	5.2
16	0.49	0.125	28.3	7	77.4	56.4	31.8	1.37	490.9	5.2
17	0.48	0.125	28.9	4	78.4	56.7	32.2	1.38	491.9	4.7
18	0.55	0.142	28.6	4	76.7	54.1	29.5	1.41	492.9	4.9
19	0.56	0.167	33.1	4	75.0	50.8	29.2	1.47	491.5	6.1
20	0.55	0.18	36.3	4	74.2	49.1	29.6	1.51	490.9	7.0
21	0.57	0.18	35.0	6	73.5	48.9	28.8	1.50	490.4	7.0
22	0.50	0.135	30.0	4	77.5	55.2	31.5	1.40	491.8	5.1
23	0.48	0.13	30.0	6	77.4	55.8	32.3	1.38	490.4	5.7
24	0.46	0.13	31.4	4	78.0	55.9	33.1	1.39	491.1	5.4
25	0.46	0.13	31.4	6	77.5	55.7	33.1	1.39	490.1	5.7
26	0.80	0.2	27.7	14	67.2	44.8	19.9	1.49	491.7	7.7
27	0.80	0.2	27.7	19	65.7	44.3	20.0	1.48	490.4	8.7
28	0.79	0.22	30.9	16	65.8	43.0	20.5	1.52	490.3	8.7
29	0.78	0.23	32.7	12	66.6	42.6	20.9	1.56	491.1	8.6
30	0.78	0.23	32.7	6	68.4	43.2	20.9	1.58	492.8	7.4
31	0.85	0.27	35.3	6	65.8	38.8	18.2	1.69	492.7	8.3
32	0.85	0.27	35.3	11	64.3	38.3	18.2	1.68	491.4	9.3
33	0.85	0.26	33.9	15	63.6	38.7	18.2	1.64	490.9	9.5

Ex. No.	Fe_2O_3 (%)	FeO (%)	Redox (%)	Co (ppm)	TLA4 (%)	TE4 (%)	TUV4 (%)	SE4	λ_D (nm)	P (%)
34	0.85	0.28	36.6	15	62.7	37.0	18.3	1.69	490.3	10.0
35	0.90	0.28	34.5	15	62.2	36.4	16.2	1.70	491.0	10.0
36	0.65	0.16	27.3	15	71.2	49.5	24.6	1.43	490.4	7.0
37	0.66	0.16	26.9	12	72.0	49.6	24.2	1.45	491.6	6.3
38	0.67	0.17	28.1	14	70.8	48.2	23.8	1.46	490.3	6.9
39	0.64	0.18	31.0	14	70.4	47.4	24.9	1.48	490.3	7.8
40	0.60	0.17	31.4	10	72.6	49.3	26.7	1.47	490.2	7.1
41	0.60	0.17	31.4	4	74.3	49.8	26.6	1.49	492.7	5.7
42	0.65	0.19	32.4	4	72.8	47.2	24.7	1.54	492.9	6.2
43	0.64	0.2	34.7	9	70.8	45.7	25.1	1.54	490.4	8.0
44	0.70	0.22	34.9	4	70.7	43.6	22.8	1.62	492.6	7.0
45	0.62	0.17	30.4	14	71.2	48.7	25.8	1.46	490.2	7.7
46	0.71	0.19	29.7	8	71.0	46.2	22.2	1.53	492.7	6.4
47	0.98	0.255	28.9	15	62.5	36.7	13.2	1.70	492.7	8.5
48	0.98	0.27	30.6	18	61.1	35.3	13.3	1.72	491.6	9.6
49	1.05	0.27	28.5	18	60.1	33.8	10.5	1.77	492.4	9.2
50	1.07	0.3	31.1	22	57.5	31.0	9.78	1.85	491.2	10.8
51	1.08	0.33	33.9	20	57.0	29.0	9.45	1.96	491.3	11.2
52	1.08	0.34	34.9	25	55.1	27.8	9.48	1.98	490.4	12.4

TABLE III

Ex. No.	Fe_2O_3 (%)	FeO (%)	Redox (%)	Co (ppm)	TLA4 (%)	TE4 (%)	TUV4 (%)	SE4	λ_D (nm)	P (%)
53	0.38	0.08	23.1	4	82.0	65.4	36.7	1.25	493.3	3.0
54	0.52	0.118	25.2	4	78.6	57.5	30.6	1.36	493.8	3.8
55	0.55	0.132	26.6	4	77.4	55.4	29.4	1.39	493.7	4.3
56	0.80	0.2	27.7	8	68.9	45.4	19.9	1.51	493.7	6.5
57	0.86	0.25	32.3	6	66.6	40.3	17.7	1.65	493.5	7.5
58	0.65	0.16	27.3	6	73.9	50.3	24.6	1.46	493.8	5.2
59	0.95	0.25	29.2	12	64.0	38.0	14.4	1.68	493.3	7.9

CLAIMS

1. A blue soda-lime colored glass composed of glass-forming principal components and of coloring agents, characterized in that it comprises from 0.15 to 1.1% by weight of Fe_2O_3, has a redox factor not exceeding 45% and presents a dominant wavelength (λ_D) of between 490 and 493 nm and a light transmission (TLA4) and an excitation purity (P) which satisfy the relationship $P > -0.3 \times TLA4 + 24.5$.

2. The colored glass as claimed in claim 1, characterized in that it has a light transmission (TLA4) of greater than or equal to 55%.

3. The colored glass as claimed in either of claims 1 and 2, characterized in that it has a light transmission (TLA4) and an excitation purity (P) which satisfy the relationship $P > -0.3 \times TLA4 + 26.5$.

4. The colored glass as claimed in any one of claims 1 to 3, characterized in that it has a dominant wavelength (λ_D) of less than or equal to 492 nm.

5. The colored glass as claimed in any one of claims 1 to 4, characterized in that it has a dominant wavelength (λ_D) of greater than or equal to 491 nm.

6. The colored glass as claimed in any one of claims 1 to 5, characterized in that it includes, as coloring agents, a compound of at least one of the elements Cr, Ce, Co, Se, V, Ti, Mn.

7. The colored glass as claimed in any one of claims 1 to 6, characterized in that it comprises amongst its coloring agents less than 0.1% by weight of TiO_2.

8. The colored glass as claimed in any one of claims 1 to 7, characterized in that it comprises less than 0.5% by weight of CeO_2.

9. The colored glass as claimed in any one of claims 1 to 8, characterized in that it comprises less than 0.13% by weight of MnO_2.

10. The colored glass as claimed in any one of claims 1 to 9, characterized in that it comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.3 - 1.1%
FeO	0.10 - 0.30%
Co	0 - 0.0040%
Cr_2O_3	0 - 0.0500%
V_2O_5	0 - 0.0500%

and has the following optical properties:

55% < TLA4 < 85%

36% < TE4 < 60%

P < 12%.

11. The colored glass as claimed in any one of claims 1 to 10, characterized in that it has a light transmission (TLA4) of greater than or equal to 70%.

12. The colored glass as claimed in claim 10, characterized in that it comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.3 - 0.7%
FeO	0.10 - 0.20%
Co	0 - 0.0020%

and has the following optical properties:

72% < TLA4 < 85%

49% < TE4 < 60%

3% < P < 9%.

13. The colored glass as claimed in claim 12, characterized in that it comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.4 - 0.6%
FeO	0.11 - 0.16%
Co	0 - 0.0015%

and has the following optical properties:

74% < TLA4 < 80%

51% < TE4 < 58%

3% < P < 7%

$\lambda_D \leq 492$ nm.

14. The colored glass as claimed in claim 10, characterized in that it comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.4 - 0.8%
FeO	0.16 - 0.23%
Co	0 - 0.0030%

and has the following optical properties:

70% < TLA4 < 77%

39% < TE4 < 50%

4% < P < 10%.

15. The colored glass as claimed in claim 14, characterized in that it comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.55 - 0.75%
FeO	0.16 - 0.23%
Co	0 - 0.0020%

and has the following optical properties:

70% < TLA4 < 74%

41% < TE4 < 48%

6% < P < 9%

$\lambda_D \leq 492$ nm.

16. The colored glass as claimed in claim 10, characterized in that it has a light transmission (TLA4) of less than 70%.

17. The colored glass as claimed in claim 16, characterized in that it comprises less than 0.01%, preferably less than 0.0050%, by weight of V_2O_5 and less than 0.0020%, preferably less than 0.0015%, by weight of Cr_2O_3.

18. The colored glass as claimed in either of claims 16 and 17, characterized in that it comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.6 - 1.1%
FeO	0.20 - 0.30%
Co	0 - 0.0040%

and has the following optical properties:

55% < TLA4 < 69%

30% < TE4 < 47%

6% < P < 12%.

19. The colored glass as claimed in claim 18, characterized in that it comprises the following percentages by weight of coloring agents, the total amount of iron being expressed in the form of Fe_2O_3:

Fe_2O_3	0.75 - 0.95%
FeO	0.22 - 0.28%
Co	0 - 0.0030%

and has the following optical properties:

63% < TLA4 < 69%

36% < TE4 < 45%

7% < P < 11%

$\lambda_D \leq 492$ nm.

20. The colored glass as claimed in any one of claims 1 to 19, characterized in that it comprises less than 1.0% by weight of Fe_2O_3.

21. The colored glass as claimed in any one of claims 1 to 20, characterized in that it forms a motor-vehicle window.

VERIFICATION OF ENGLISH LANGAUGE TRANSLATION

In the matter of entry into the U.S. National Stage of PCT application PCT/EP00/01394.

I, Daphné Derouane certify that I am conversant with the English and French languages and that the attached English language text is a true and correct translation of the French langauge application PCT/EP00/01394 filed 21 February 2000.

Executed at Jumet, Belgium, on the 20th day of August, 2001, under penalty of perjury of the laws of the United States.

Daphné Derouane

Docket No.:4004-022-30

Combined Declaration and Power of Attorney

WE (I) the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

BLUE SODA-LIME GLASS

specification of which

☐ is attached hereto.

☐ was filed on _____

as Application Serial No. _____

and amended on _____

■ was filed as PCT international application

Number PCT/EP00/01394

on February 21, 2000

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
99103543.7-2111	Europe	February 24, 1999	■ Yes ☐ No
			☐ Yes ☐ No
			☐ Yes ☐ No
			☐ Yes ☐ No

We (I) hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below.

(Application Number)	(Filing Date)
(Application Number)	(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. §120 of any United States application(s), or §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)

And we (I) hereby appoint Steven B. Kelber, Reg. No. 30,073; Marc R. Labgold, Ph.D., Reg. No. ~~34,651;~~ Jerold I. Schneider, Reg. No. ~~24,765;~~ Paul C. Kimball, Reg. No. 34,641; Laura A. Kelly, Reg. No. ~~38,435;~~ Wilburn L. Chesser, Reg. No. ~~41,668;~~ James M. Heintz, Reg. No. ~~41,828;~~ and D. Nammo, Reg. No. ~~42,024;~~ Perry E. VanOver, Reg. No. ~~42,197;~~ Amy L. Miller, Reg. No. ~~43,804;~~ Raymond Millien, Reg. No. ~~43,806;~~ Kenneth Vu, Reg. No. ~~46,323~~ and Christopher W. Raimund, Reg. No. ~~[illegible]8~~, as our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to Supervisor, Patent Prosecution Services, Piper Marbury Rudnick & Wolfe LLP, 1200 Nineteenth Street, N.W., Washington, D.C. ~~20036-2412~~.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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Date